ストラティファイドCdS光触媒と硫化水素を利用した太陽エネルギー変換に関する研究

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論 文 内 容 要 旨

Splitting of hydrogen sulfide using sunlight is a useful reaction to produce hydrogen. Hydrogen sulfide is a harmful gas that is generated from volcanic zone, natural hot springs, and from petroleum processing and sewage treatment plants. In this study, alkaline sulfide solution, which is prepared by dissolving hydrogen sulfide into alkaline water, is selected as the reaction medium. The advantages of using alkaline sulfide solution to hydrogen generation reaction are follows:

- Removing the odor of hydrogen sulfide.
- The concentration of hydrogen sulfide can be enhanced by dissolving the gas in alkaline solution.
- The photolysis voltage of alkaline sulfide solution is lower than that of water.
- Oxygen and Chlorine will not be generated in the hydrogen generation reaction.

Hydrogen generation system using alkaline sulfide solution could be used not only for hydrogen generation, but also for improving the quality of water and recover heavy metals from waste water and sea water by reacting the same with spent solution from hydrogen evolution reaction.

The aims of this study are (a) to design of a photocatalyst particle that generates hydrogen effectively by splitting alkaline sulfide solution and (b) to determine the optimum condition of the reaction medium.

This thesis is composed of five chapters. In the first chapter, the aim and significance of this study are described. In the second chapter, the structure and the reactivity of stratified sulfide semiconductor particle prepared by using oxide or hydroxide as precursor is described. In the third chapter, the factors that contribute to the high activity of stratified semiconductor particle are verified. In the preparation process of stratified particle, the color of the particle changes from white or yellow to black and this phenomenon is believed to improve the reactivity. The relation between the change of color to black and hydrogen generation reactivity is described. In the fourth chapter, the experimental conditions are optimized for the hydrogen generation reactivity. And

various phenomena that affect the reaction are considered, and a new reaction model is proposed. Conclusion is summarized in chapter five.

In the second chapter, the details of the preparation of the highly photocatalytic sulfide semiconductor particles, for the generation of hydrogen from alkaline sulfide solution, by using oxide and hydroxide as a precursor are presented. The particles prepared by this method are called "stratified particle". In this study, two design concepts have been used to prepare photocatalyst. Firstly, since the specific surface area is an important factor in photocatalytic reaction, efforts were made to prepare fine semiconductor particles. By decreasing the particle size, the carry over factor of the photoexcited electron on the reaction surface is expected to increase. Secondly, effort was made to create contact between semiconductor and metal. This contact will create an electric field gradient within the particle and assist the separation of photoexcited electrons and holes. In the study, semiconductors ZnS and CdS were selected for their well-known activity of hydrogen generation in alkaline sulfide solution.

Stratified ZnS particle was prepared by using ZnO as precursor. Here, ZnS particles were precipitated around the precursor to form a capsule like structure. This shape was confirmed from the FE-TEM image. It is supposed that Zn metal exists inside the capsule and forms the metal-semiconductor contact. This 'stratified ZnS' particle generated hydrogen actively than the ZnS fine particle prepared by the co-precipitation technique.

The activity of ZnS particle supplied by Kojundo Chemical, 5N was enhanced by oxidizing the surface of ZnS by using H_2O_2. This fact suggests that the coexistence of oxide and sulfide is important to improve the activity of ZnS semiconductor.

Stratified CdS particle prepared using $Cd(OH)_2$ as precursor shows capsule structure as observed in the case of ZnS. The basic difference between stratified CdS and ZnS is that the photocatalytic activity of CdS is low. However, the activity is enhanced very much when the CdS particle is supported with Pt by photo-deposition method. This Pt-deposited stratified CdS particle also shows higher activity than CdS particle prepared by the co-precipitation method.

In both ZnS and CdS cases, the metal sulfide semiconductor particle prepared via metal oxide or hydroxide showed higher activity than the sulfide particles prepared by using the co-precipitation method. It is confirmed that the unique preparation method proposed here is effective to improve the activity of hydrogen generation. CdS particle could decompose H_2S in visible light. The successful synthesis of stratified CdS particle is a major step towards the realization of the hydrogen generation system using sunlight.

In the third chapter, the reason for the high activity of CdS particles in alkaline sulfide solution is discussed.

Photo-irradiation process is utilized during the preparation of stratified particles, and the processed particle turns black in color. The reason for the color change is considered to be due to the reduction of the remaining metal oxide or hydroxide precursor by the photo-excited electron from semiconductor and deposited as metal on the surface. This difference in color was observed between stratified and co-precipitated particles. To correlate the color change phenomenon to the hydrogen generation, the sample that was free of the precursor prepared by HCl

treatment was compared with the stratified particle. The following facts were confirmed.

- The activity of the stratified ZnS particle was improved whenever the change in color from white to black was shown.
- Stratified CdS particle shows little activity in spite of the color change from yellow to black.
- The activity of the Pt-deposited stratified CdS particle improved along with the color change.

This fact is construed as follows: The reason for the stratified CdS particle not showing the activity without Pt is that CdS has lower energy level of conduction band than ZnS and hence does not have enough reducing power to produce hydrogen. Therefore, the metal with low hydrogen overpotential, such as Pt, is needed to produce hydrogen. The color change phenomenon comes from the photodeposited Zn or Cd metal. These metals are supposed to have low possibility of working as reduction site because of their high hydrogen overpotential. Hydrogen overpotential is supposed to be one of the reasons that the Cd-metal supported CdS with less reducing power shows low activity. To improve photocatalytic activity, it is needed that both reduction and oxidation reaction take place. It is believed that oxidation power of sulfide semiconductor is weaker than that of the oxide semiconductor. It is thought that Zn and Cd metals work as oxidation site and improve the oxidation of sulfide ion.

It is confirmed that the samples that did not undergo color change show low activity in both stratified ZnS and CdS particle cases, and the color change phenomenon effects positively and improves the activity of hydrogen generation.

It seems that the contact between metal and semiconductor is important to improve the activity. The enhancement in the overall efficiency of the photocatalytic reaction was attempted by improving the contact between metal and semiconductor by heat treatment, and by optimizing the photodeposited Pt metal concentration. During heat treatment, the activity decreased with rising temperature. It is supposed that photocatalyst itself transformed by heat treatment. On the other hand, the photocatalytic activity increased with Pt ion concentration. However, the increment was minimal at concentrations above 0.5wt%.

In the fourth chapter, the condition of the reaction medium was optimized. Considering various phenomena observed in the experiments, a new reaction model is proposed.

The influence of sulfide ion concentration on the hydrogen evolution was examined. The optimal the value of sulfide ion concentration was around 0.1M. At higher concentrations, photocatalyst transformed and its activity decreased.

$$2H_2O + 2S^{2-} \rightarrow H_2 + S_2^{2-} + 2OH^- \qquad (1)$$

The consumption of sulfide ion against the amount of hydrogen generation is measured by ion chromatography. The relation between sulfide ion consumption and the amount of hydrogen generated was almost proportional. However, the amount of hydrogen generated was determined to be more than what could be expected from equation 1. At low Na_2S concentration, the precipitation of sulfur is observed and this cannot be explained by this equation. Disulfide ions are yellow in color and absorb the light used to excite CdS. Thus, the possibility of the oxidation of disulfide ion was considered. To prevent the formation of disulfide ions, sulfite ion was introduced into the solution. Here, the disulfide ions changed to colorless thiosulfate ions. Thus, a solution

containing sulfide and sulfite ions is considered ideal. The above results also explain the excess amount of hydrogen evolved.

In this study, the hydrogen generation reaction in alkaline sulfide solution is believed to have been caused by the dissociation of H-S bond and a new reaction model is proposed from a different viewpoint based on previous studies. The bond dissociation energy of O-H is 427 ± 1(kJ/mol), as against 351 ± 17(kJ/mol) for S-H bond. The difference in bond dissociation energy is equal to 0.8eV per molecule. Based on this difference, it seems reasonable to assume that hydrogen generation does not occur from the dissociation of OH^- ion or H_2O but rather from the dissociation of HS^- ion. The unique point about the proposed reaction model is that it defines the reduction site. HS^- ion is described as the reaction medium at the reduction site, but in total, the reaction at the reduction site occurs through the decomposition of water. However, this is different from the direct decomposition of water.

H in H_2O is moved to S that has lower electronegativity than O, and S-H bond is formed. The dissociation energy of this bond is less than that is necessary to split water directly. In this reaction, S seems to act as the proton pump.

The possibility of transformation of stratified CdS particle to some other form at high concentration and its influence on the photocatalytic activity were studied. From this study, the optimal concentration of sulfide ion is around 0.1mol/l. Thus, the sulfide ion concentration in the experiment to determine the lifetime of photocatalyst was set at 0.1mol/l. The result of this study suggested that the sulfide ion concentration is critical not only for the hydrogen generation rate but also for the lifetime of photocatalyst. Even for 0.1M Na_2S solution, the decrease of photocatalytic activity is observed and suggested that with the hydrogen generation reaction may not be photocatalytic reaction is concerned. To confirm this, the turnover frequency is calculated, which is found to be 24. As this value is more than 1, hydrogen generation can be concluded to be a photocatalytic reaction.

To summarize, stratified particles prepared using oxide or hydroxide show higher activity than the particles prepared by co-precipitation. Stratified particle consisted of metal-deposited sulfide semiconductor, arranged like a capsule. This structure seems to improve the separation of reaction sites and prevent the recombination of photoexcited electron and the hole. From the viewpoint of the reaction medium, alkaline sulfide solution containing sulfite ion is considered to be the best because it prevents the precipitation of sulfur produced from the oxidation of disulfide ion. And also, the concentration of alkaline sulfide solution was found to influence the lifetime of the photocatalyst. Optimal concentration is around 0.1M. In hydrogen generation reaction, the dissociation energy of H-S bond is lower than that of the H-O bond. It is essential to move H from O to S in static reaction to make photocatalytic hydrogen generation easier. In this viewpoint, sulfur acts as proton pump.

It is expected that the results obtained in this study are important for the establishment of a hydrogen generation system by splitting H_2S using sunlight.

論文審査結果の要旨

本研究は、硫化水素と太陽エネルギーを利用した水素製造システムの構築を目指している。水素は、理想的なエネルギーとして注目されているが、自然界には単独で存在しないため、水素化合物にエネルギーを加えて分解し取り出さなければならない。本研究では、水素源である硫化水素を太陽エネルギーにより効率的に分解するためのストラティファイドCdS光触媒の調製、その粒子構造と触媒活性の関係、さらに硫化水素アルカリ溶液中での反応過程について、それらの結果を全５章にまとめたものである。

第１章は序論であり、水素エネルギーとその製造方法、光触媒を用いた水素生成反応ならびに自然界の光合成、そして硫化水素の分解による水素生成など、研究背景を示し、最後に本研究の目的と意義について述べている。

第２章は、酸化物・水酸化物を前駆物質とした硫化物半導体微粒子の調製について述べている。光触媒のナノ粒子化に伴う利点と欠点を示し、欠点を補うために光触媒のストラティファイド構造化を提案している。この提案を証明するため、ストラティファイドZnS光触媒を調製し、その活性評価ならびにナノレベルでのストラティファイド化の達成をXRD、XAFS、TEMなどの測定により証明した。さらに、太陽光利用するため、CdSストラティファイド光触媒を開発し、太陽光のもとでの水素生成を可能にした。また、この光触媒の詳細な性能評価を行っている。

第３章では、ストラティファイド構造を制御し、様々な調製過程で光触媒を機器分析により評価し、光触媒活性の発現理由を構造学的観点から研究を行っている。その結果、水素の発生サイトを形成する金属ナノ微粒子の状態と担持量が、活性に影響を与えることが判明した。その結果をもとに、触媒活性向上のための試みを行い、量子効率最大１６％という、世界最高性能の光触媒を開発した。

第４章では、硫化アルカリ溶液中の光触媒反応について詳細な研究を行っている。溶液濃度変化に伴う水素生成速度の変化や反応中に見られる白色物質の同定などから、これらの現象を満足するアルカリ水溶液中の光触媒反応モデルを提案している。この反応モデルでは、これまでの報告とはことなり、水素生成に水が関与することが判明した。さらに、本章では、触媒寿命と溶液濃度の関係ならびに触媒性能を示すターンオーバー数を求めている。

第５章は、結論であり、これまでの研究結果を総括し、今後の展開を詳細に議論している。

以上、本論文では、光触媒をストラティファイド化により性能を向上し、その触媒活性と触媒構造との関係を示した。そして、硫化アルカリ溶液中の光触媒反応モデルを構築し、さらに有害物質である硫化水素を無害化しながら水素を製造できることも示した。そして、硫黄を循環することで、水から水素を製造するシステムが完成することも提案した論文であり、環境科学ならびに理学や工学の発展にも寄与するところが大きい。

よって，本論文は博士(学術)の学位論文として合格と認める。